Layered Ultrathin Proton Conductive Film Based on Polymer Nanosheet Assembly

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Experimental details

Materials

N-dodecylamine, acryloyl chloride triethylamine, and 2-acrylamide-2-methylpropanesulfonic acid were purchased from Tokyo Chemical Industry (TCI) Co., Ltd and used as received. 2,2'-azobis(isobutylronitrile) (AIBN) was purchased Wako Pure Chemical Industries, Ltd and recrystallized from methanol. Dehydrated chloroform and THF were purchased from Wako Pure Chemical Industries, Ltd and used as received. *N*-dodecylacrylamide was synthesized by the reaction of acryloyl chloride with dodecylamine, in the presence of triethylamine in chloroform. A mixture of dodecylamine (2.5 g), triethylamine (2.17 mL) and dehydrated chloroform (130 mL) was cooled at 0 ˚C in ice-water bath. Acryloyl chloride (1.26 mL) was then added dropwise to the mixture under stirring. The reaction mixture was allowed to stand at room temperature for 3 h. Then, Then, the mixture solution was washed with dilute hydrochloric acid, followed by NaHCO3 aqueous solution (10wt%) and water. The chloroform layer was dried over anhydrous Na2SO4. After being filtered and evaporated, the residue was recrystalized from chloroform/hexane. poly(*N*-dodecylacrylamide-*co*-2-acrylamide-2-methylpropanesulfonic acid), was prepared by free radical copolymerization of DDA with AMPS in THF/H_2O mixture solvent at 60 ˚C using 2,2'-azobis(isobutylronitrile) (AIBN) as a thermal initiator. The molar ratio of DDA and AMPS was 4:1, and the total monomer concentration was 0.2 mol L^{-1}. The polymer was purified by precipitation in a large excess of acetonitrile from chloroform solution and dried under vacuum at room temperature. The mole fraction of AMPS in the copolymer was determined by elemental analysis using the atomic content of sulfur (2.06%).

Measurements

The number average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined

using a gel permeation chromatograph (GPC-8020; Tosoh Corp.) with a polystyrene standard. The mobile phase was THF with a flow rate of 0.2 mL/min. The absorption spectra were measured using UV-vis spectrophotometer (U-3000; Hitachi Ltd). FT-IR spectrum was obtained using an FT-IR spectrometer (FT/IR4200; Jasco Corp.). π-A isotherm measurement and the deposition of p(DDA/AMPS) monolayer were carried out with computer-controlled Langmuir trough (FSD-50 and 51; USI). Distilled and deionized water (>17.5 MΩ cm, CPW-101; Advantec) was used as the subphase. The surface morphology of the polymer film was measured with atomic force microscope (AFM) (SPA-400 SII; NanoTechnology Inc.). The silicon cantilever with spring constant k = 20 N/m (SI-DF 20; Olympus Corp.) was used in non-contact mode. Thermogravimetric analysis (TGA) was performed under N_2 atmosphere at heating rate of 10°C/min using TGA-50. The polymer monolayer was compressed at a rate of 15.0 cm^2/min.

Sample preparation

The silicon, quartz and glass substrates that were used as a deposition substrate were cleaned by treatment with a UV-O_3 cleaner (NL-UV253; Nippon Laser and Electronics Laboratory) and hydrophobicized by immersion of the substrates into a ca. 1×10^{-6} M octyltrichlorosilane (Tokyo Chemical Industry Co., Ltd.) chloroform solution. Twenty layers of p(DDA/AMPS) were deposited onto CaF_2 substrate to measured the FT-IR spectrum. The spectrum was measured by transmission mode.

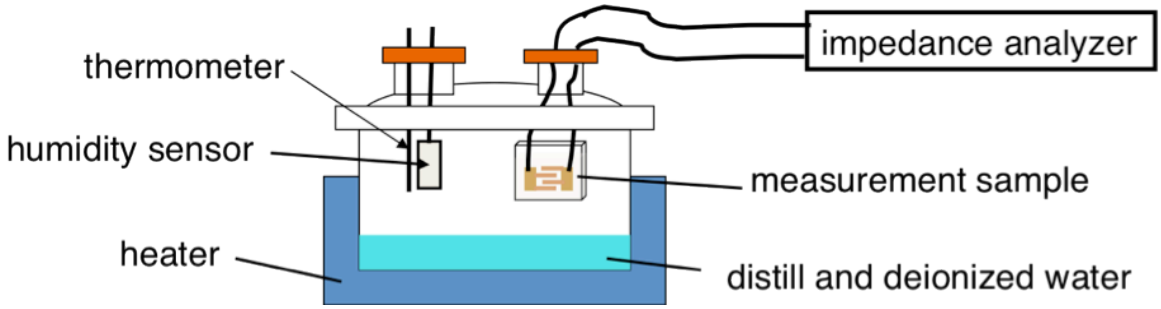

Fig. S1 Apparatus for the proton conductivity measurements of p(DDA/AMPS) films

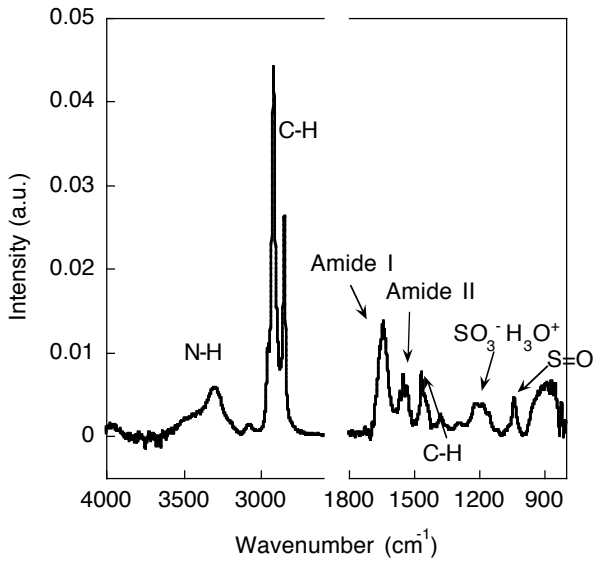

Fig. S2 FT-IR spectrum of 20 layers of p(DDA/AMPS) multilayer film.

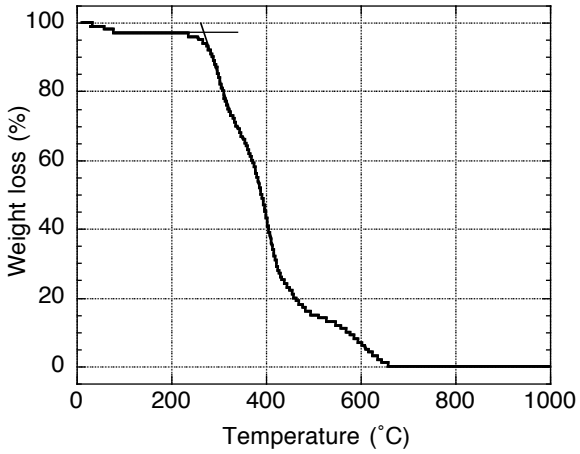

Fig. S3 TGA curve of p(DDA/AMPS).

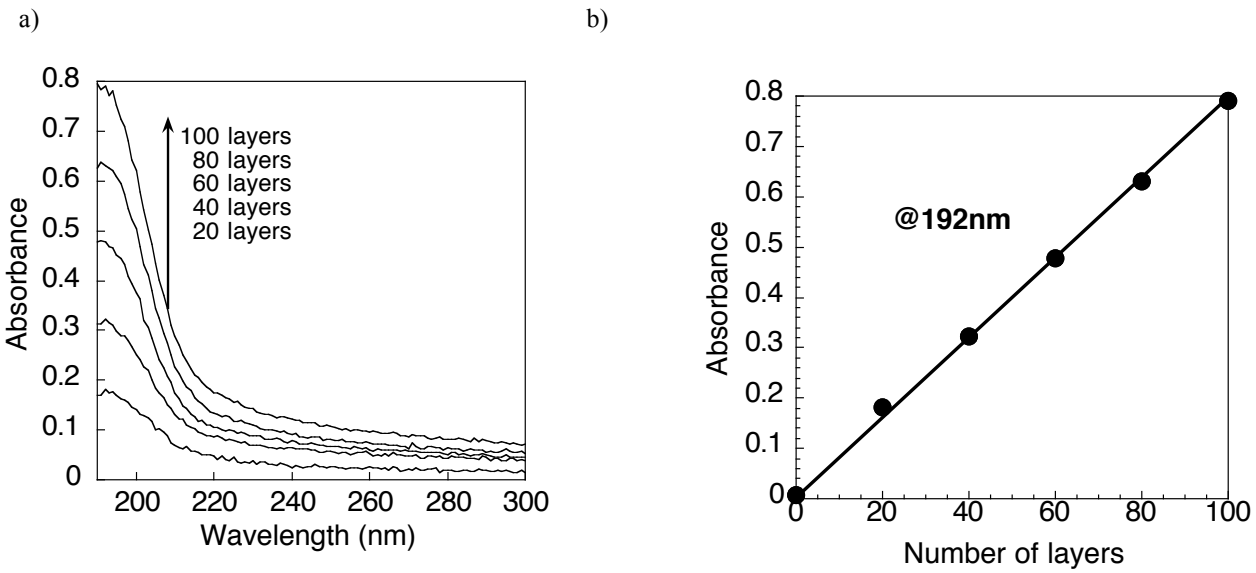

Fig. S4 (a)UV-vis spectra of p(DDA/AMPS) polymer nanosheet with different numbers of layers. (b) Absorption intensity at 193 nm as a function of the number of layers

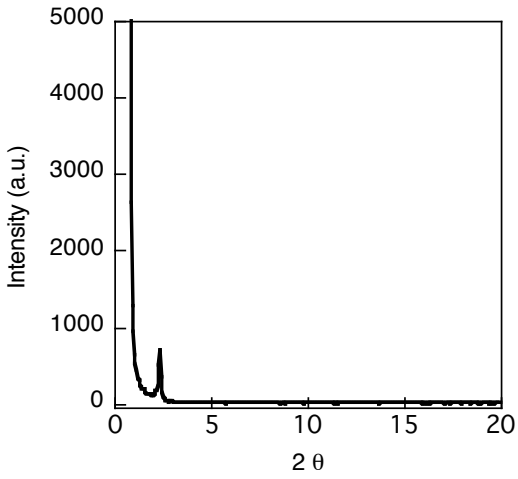

Fig. S5 XRD pattern for 30-layer p(DDA/AMPS) polymer nanosheet multilayer film on a silicon substrate.

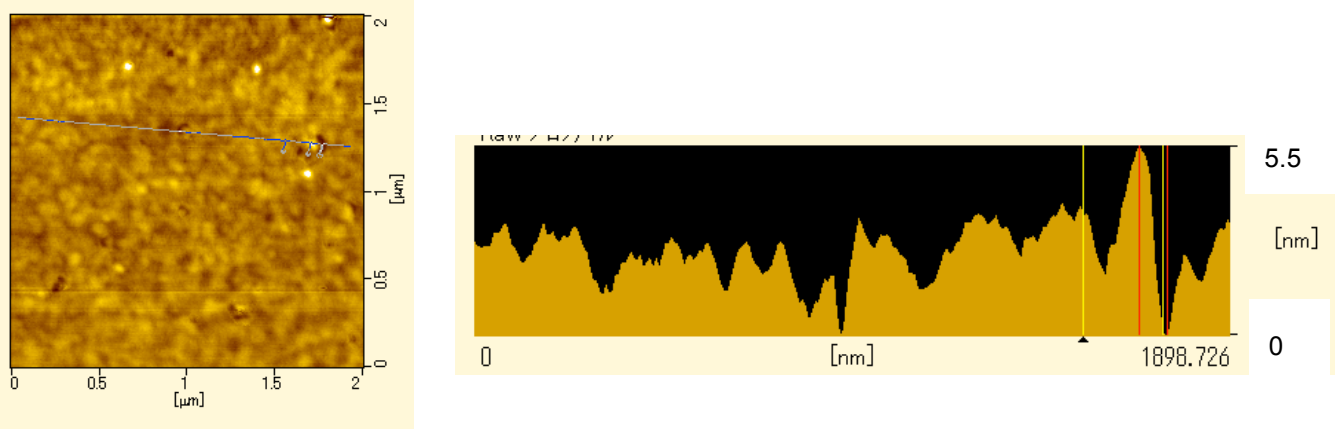

Fig. S6 AFM image of and the height profile 2-layer p(DDA/AMPS) polymer nanosheet on a silicon substrate

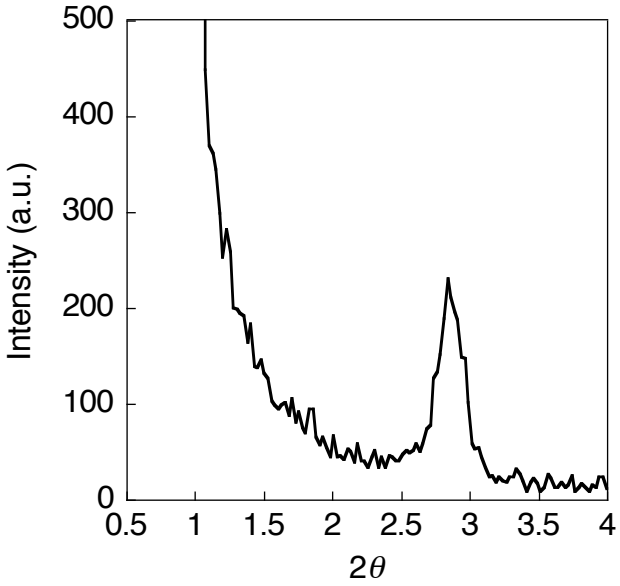

Fig. S7 X-ray diffraction patterns for a 30-layer p(DDA/AMPS) polymer nanosheet assembly after the conductivity measurement at 70 ˚C.